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Synthesis of Titania coated Alumina Particles by a Hybrid Sol-gel Method

A.D. Schmidt[1], S.B. Majumder[2], P.S. Dobal[2], R.S. Katiyar[2], and D.C. Agrawal[3]
[1]Goshen College, Department of Chemistry, Goshen, IN, USA
[2]Department of Physics, University of Puerto Rico, San Juan, PR 00931-3343
[3]Materials Science Program, Indian Institute of Technology, Kanpur, 208016, India

ABSTRACT

Modifying their surface with a coating of another ceramic material can dramatically alter the properties of ceramic particles. In the present work we have demonstrated that the Al_2O_3 particles can be successfully coated by TiO_2 using a novel sol-gel technique. The nature of these coatings was predicted on the basis of scanning electron microscopy imaging in conjunction with the micro-Raman scattering measurements. The surface morphology of these particles shows that either individual or group of sub-micron alumina particles are coated with the nano-crystalline titania particles. The thickness of the titania coating could be varied by changing the precursor sol concentration. Amorphous titania was converted to anatase phase at 400°C and upon further heating it started transforming to rutile phase, and both these phases coexisted in the coated particles that were heat treated up to 800°C. The mechanical strength of the titania coating was measured qualitatively by ultrasonicating the coated powders for longer duration to observe that titania coatings are strongly adhered with the alumina particles.

INTRODUCTION

Coating a ceramic particle with another material can be useful for a number of applications. One such use is to uniformly coat the ceramic particle with organic binder in order to disperse it uniformly into the ceramic matrix.[1]. The other use has been to distribute sintering aid in ceramic matrix, thus bohemite coating is reported to enhance the green state plasticity and sintered density of Si_3N_4 ceramics [2]. Coating silica on alumina particles are found not only to improve the sintered density of alumina, but also form mullite, an important high strength ceramic compound [3]. In colloidal processing of ceramic composite the interaction forces can be altered by changing the surface properties of ceramic particles by coating with another ceramic material to achieve hetero-coagulation [4]. Sol-gel processing has been found to be effective in coating the ceramic particle with an amorphous gel coating of another ceramic. Metal alkoxide or salts are used as precursor material to prepare an amorphous gel layer around the ceramic particles [5-6]. The effectiveness of the gel coating on ceramic particles are demonstrated through TEM analysis, however, the nature of these coatings after calcinations have not been studied adequately [5]. In this work we have studied the nature of titania coating on alumina particles by calcining these coated particles in a wide range of temperature (as dried at 80°C to 800°C) in air. Titania coating is expected to enhance the sinterability of alumina and these powders could be used as low loss microwave dielectric material. The nature of titania coating has been studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and micro-Raman spectroscopy. The experimental results clearly indicate the effective coating of

alumina by titania nano-particles. It is also demonstrated qualitatively that the titania is reasonably well adhered to the alumina particles.

EXPERIMENTAL DETAILS

Ti sols (concentration varied from $1X10^{-2}$ M to $1X10^{-3}$M) was prepared by dissolving Ti-isopropoxide in acetic acid (1:1 weight percent). About 2 gm of alumina powders were ultrasonically dispersed in about 30 ml acetic acid to form a stable suspension. The isoelectric point (IEP) of alumina is about 9.2 and therefore maintaining the pH of the suspension in acidic range (~3-4) yield excellent dispersion of alumina. The acetic acid chelated Ti sol was added drop-wise into alumina suspension at room temperature with continuous stirring. The resultant suspension was allowed to settle, and the lighter particles, excess sol and solvents were decanted to separate the heavier particles with an amorphous gel layer. The resultant paste was transferred in a petridish (kept on an ultrasonicate bath) and dried by flowing compressed air at room temperature. The dried powders were heat treated in a temperature range of 200 to 800°C for 2h in air maintaining a heating rate of $5°Cmin^{-1}$. Differential thermal analysis in conjunction with Fourier transformed infra-red spectroscopy (FTIR) of powders heat treated at different temperatures for 2 hours, were performed to characterize the thermal events as a function of temperature. The nature of the coating was analyzed by a combined XRD and SEM studies in conjunction with micro-Raman spectroscopy.

RESULTS AND DISCUSSIONS

Figure 1 shows the FTIR spectra of titania gel coated alumina particles (a) as dried, calcined at (b) 400°C and (c) 800°C for 2 hours in air. The acetate bands attached with Ti (at about 1400 and 1520 cm^{-1}) along with other bending and stretching modes (assigned in Fig. 1a) are clearly seen in as dried powders, however, their absence in powders annealed at higher temperatures (Fig. 1b and 1c) indicated that the organics are completely removed at about 400°C. This is also supported by the DTA analysis (not shown).

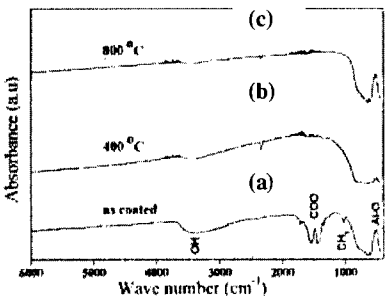

Figure 1 FTIR spectra of titania coated alumina particles calcined at different temperatures

The typical crystallization behavior of titania coating is shown in Fig.2a. As revealed from the XRD results, the titania crystallizes into anatase (tetragonal, indexed according to JCPDS file 21-1272) phase at 400°C. The anatase to rutile (tetragonal File 21-1276) transformation initiates at about 600°C (or less) and both these phases coexist till 800°C. The ratio of rutile: anatase phases, as a function of annealing temperature, was calculated from the X-ray diffractograms and it was shown that the rutile phase content increases with the increase in calcinations temperature for all concentrations of titania precursor sols (Fig.2b). The relative phase contents were calculated as follows : the (101) anatase peak was deconvoluted

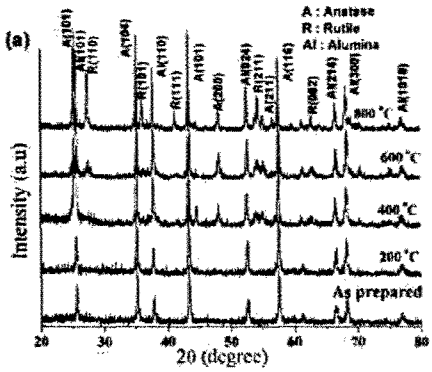

Figure 2(a) X-ray diffractograms of titania coated alumina particles calcined at different

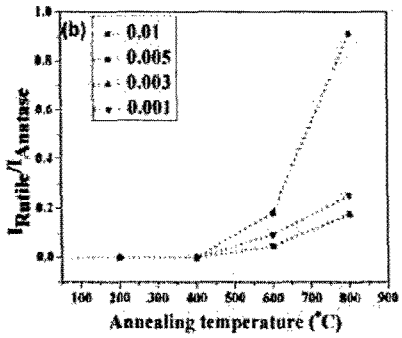

Figure 2(b) Variation of rutile:anatase phase contents as a function of calcination temperature

from (012) diffraction peak of alumina using Pearson VII function. The rutile (110) peak was also fitted using the same function and the ratio of the integrated area of (110) rutile peak: (101) anatase peak was taken to be a measure of the rutile: anatase phase content. The dramatic anatase to rutile conversion (particularly in powder calcined at 800°C) for $5X10^{-3}$M titania coated composition is not well understood. Probably, other factors such as grain growth etc also influence the intensity ratio, and therefore, the ratio of phase contents are not strictly represented only by the intensity ratio of the diffraction peaks of corresponding phases.

X-ray diffraction analysis, however, failed to predict the nature of titania coating on alumina particles. The possibilities of this kind of coating approach have schematically been shown in Fig. 3. Dipping alumina particles in titania sol and subsequent ultrasonication is assumed to uniformly coat alumina with amorphous titania gel. Upon annealing three kind of situations are predicted, crystalline titania are separated from alumina particles (case I), titania could either partially (case II) or fully (case III) coat alumina particles. To observe the nature of titania coating, the surface morphology of the calcined coated powders were characterized by SEM. For this purpose a dilute dispersion of calcined alumina powders and titania coated alumina was made in isopropanol solvent. The concentration of particles was such that it gives a turbid appearance. The pH of the suspension was maintained slightly acidic; and since the IEP of TiO_2 and Al_2O_3 are 6 and 9.2 respectively it is expected that the repulsive force between oxide particles avoid coagulation [7]. The stable suspension drop was taken out by a micro-pipette and put on a mirror polished aluminum stub and the solvents were allowed to evaporate at room temperature. This avoids any undesired particle agglomeration due to forced drying. Fig. 4 (a) shows the micrograph of calcined uncoated alumina. Uncoagulated alumina

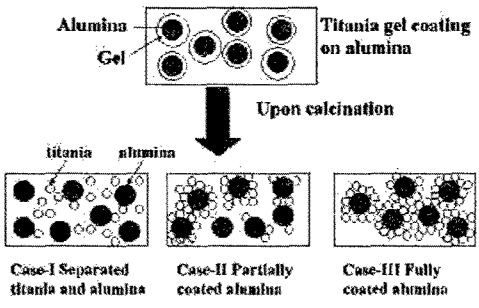

Figure 3 Schematic diagram of the probability of different kinds of coating

particles, in the size range of 0.4-0.5μm, are seen in the micrograph. Fig. 4(b) shows the TiO_2 coated alumina (TiO_2 coating was made from 0.01 M/L precursor sol). It is clearly seen that alumina particles are coated completely with TiO_2 particles. It is worth mentioning here at this point that both these micrographs are the representatives of several SEM pictures taken in many different samples. However, at this stage we are not ruling out the possibility of alumina partially coated with titania, as shown schematically in Fig. 3 (case II).

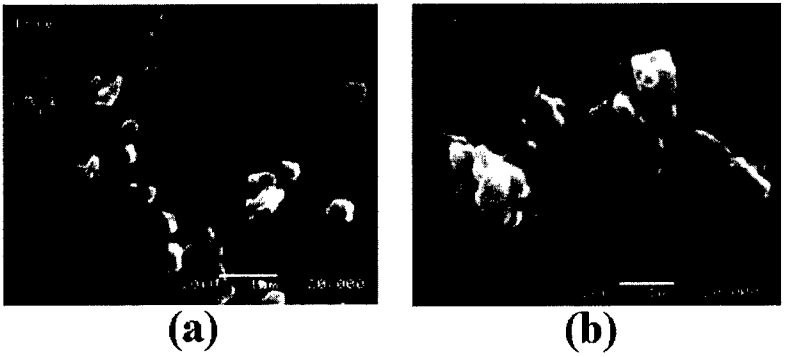

Figure 4 SEM micrographs of (a) bare and (b) 0.01M titania coated alumina particles both calcined at 800^0 C for 2 h

Micro-Raman spectroscopy has been used as an effective characterization tool to draw a definite conclusion about the nature of titania coating on alumina. Figure 5 shows the Raman spectra of as prepared and titania coated alumina, heat treated at different temperatures for 2h in air. Note that up to 200°C the Raman spectra are featureless indicating the alumina particles are fully coated with the titania gel since no characteristics band of alumina is apparently observed. The titania coating is crystallized into anatase phase upon heat treatment at higher temperature as indicated by the Raman spectra and the absence of any characteristic band of alumina clearly indicated that alumina particles are fully coated with titania particles. We have done these measurements for other titania coated particles prepared with different titania alkoxide concentration and the outcome was identical as reported in Fig.5. Also Raman measurements were performed in different regions of these samples and the results show that the alumina particles are completely coated with titania as predicted in Fig. 3 (case III).

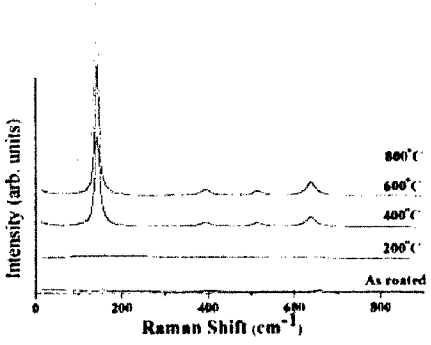

Figure 5 Raman spectra of titania coated alumina annealed at various temperature for 2h.

Finally, we tested qualitatively the strength of the adhesion of the titania coating on alumina particles. For this purpose a dilute suspension of coated powders were ultrasonicated for extended period of time (up to 2h) and Fig. 6 shows the Raman spectra of coated powders prepared from 0.01 and 0.001 M/L Ti sol. As shown in the Figure, the appearance of only titania bands in the recorded Raman spectra even after 2 h of ultrasonication, clearly indicates the strong adherence of the

coating on alumina. However, the appearance of a very broad band of alumina in case of titania coated from the thicker sol indicates that dilute concentration of the coating sol could have more effect for efficient coating. More systematic studies are required to understand these issue better.

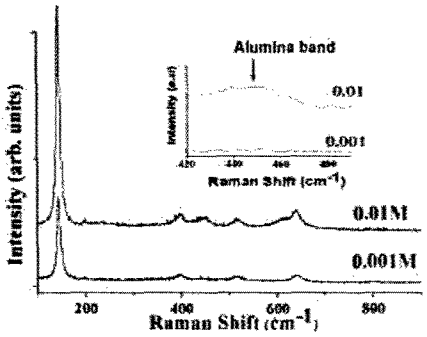

Figure 6 Raman spectra of titania coated alumina after ultrasonication for 2h

CONCLUSIONS

A hybrid sol-gel technique has been described to prepare titania coated alumina powders. Through a combined study of SEM and micro-Raman we have demonstrated that alumina particles are completely covered by titania. Preliminary characterizations show that these coatings are reasonably well adhered to alumina particles. More systematic studies are required to understand the growth behavior of titania as a function of precursor sol concentration and heat treatment conditions. Moreover, the sinterability and the high frequency (> GHz) dielectric characteristics of these materials are also interesting to study for the possible use in microwave devices.

ACKNOWLEDGMENTS

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